REPORT DOCUMENTATION PAGE

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5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

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AFRL/PRS
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Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

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14. ABSTRACT

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MEMORANDUM FOR PRS (Contractor Publication)

FROM: PROI (TI) (STINFO) 25 October 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2000-207**
Drake, Greg; Tollison, Kerri (ERC), "The Synthesis and Characterization of New Energetic Salts"

HEDM Contractors Conference (Park City, UT, 23-26 Oct 2000) **(Statement A)**
(Deadline: 20 Oct 2000 – PAST DUE)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
Comments:____________________

Signature ____________________ Date __________

2. This request has been reviewed by the Public Affairs Office for: a.) appropriateness for public release and/or b) possible higher headquarters review
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4. This request has been reviewed by PRS for: a.) technical accuracy, b.) appropriateness for audience, c.) appropriateness of distribution statement, d.) technical sensitivity and economic sensitivity, e.) military/ national critical technology, and f.) data rights and patentability
Comments:____________________

APPROVED/APPROVED AS AMENDED/DISAPPROVED

____

PHILIP A. KESSEL Date
Technical Advisor
Propulsion Science and Advanced Concepts Division

Cleared (PA)____________________
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Notified (PA)____________________
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The Synthesis and Characterization of New Energetic Salts

2000 High Energy Density Matter
United States Air Force Contractor's Review

Wendesday October 25, 2000
Park City Utah

Greg Drake; Kerri Tollison*; Tom Hawkins; Adam Brand; Milton Mckay; Ismail Ismail*

AFRL/PRSP & *ERC, Inc., 10 East Saturn Boulevard, Bldg 8451
Air Force Reseach Laboratory, Edwards Air Force Base CA 93524-7190

Monopropellant Goals: Make stable, highly energetic, dense materials, which are balanced in respect to the formation of the expected exhaust product with self contained oxygen atoms, during a combustion process.

$$\mathbf{C_vH_uN_yO_zX_q \longrightarrow CO + CO_2 + H_2O + N_2 + HX + \Delta Hc}$$

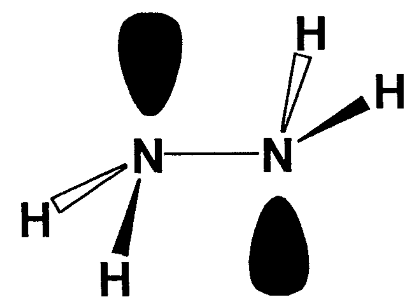
New materials has several significant hurdles to pass before it can become a legitimate propellant candidate.

- "Ease" of synthesis 3 steps or less from commercially available materials
- Thermal stability- Material must have reasonable stability, usually with a DSC onset of > 150° C
- Extended thermal stability- material must lose less than 1% per day at 75° C
- Safety- Friction and impact characteristics must be acceptable. Insensitivity is ideal, but usually be less sensitive than HMX
- Card Gap Test – Determines if the material will be classified 1.1(propagates explosion) or 1.3(non-propagation of explosion)

Conclusion: Difficult to get a material from an idea to reality and pass all of these tests!!

Hydrazine is currently the state of the art in many satellite altitude and attitude systems. It is usually decomposed over a heated catalyst bed.

$$5\,N_2H_4 \xrightarrow{\text{Catalyst bed}} 4\,NH_3 + 3\,N_2 + 4\,H_2$$



Molecular weight: 32.04 g/mole

Density at 25° C = 1.00 g/cm^3

ΔHf = +14 kcal/ mole

Vapor Pressure at 25°C = 14 torr

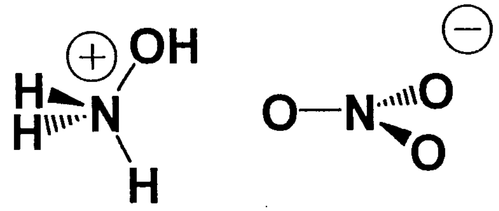
I_{sp} (300 p.s.i.; 50:1 expansion ratio) = 233 seconds

<u>Advantages:</u> industrially made in large quantities; technology already well proven with active catalyst; relatively low flame temperature

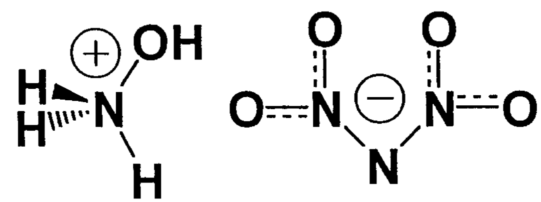
<u>Shortcomings:</u> relatively low density; Extreme toxicity, especially through inhalation; vapor pressure is approximately twice that of water.

G. P. Sutton <u>Rocket Propulsion Elements An Introduction to the Engineering of Rockets 6th Edition.</u> John Wiley & Sons. New York, NY. 1992, 257.

The work of the current group comes as an extension of an idea of Dr. Tom Hawkins (AFRL/PRSP), which, through the use of energetic salts, many of the inherent shortcomings of hydrazine can be resolved.



Hydroxylammonium nitrate (HAN)
Melting point: 39-40° C
Density: 1.685 g/cm^3(l)



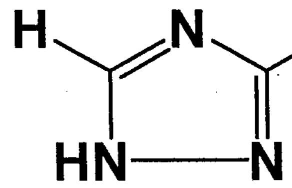
Hydroxylammonium dinitramide (HADN
Melting point: 27°C
Density: 1.733 g/cm^3

<u>Advantages:</u>

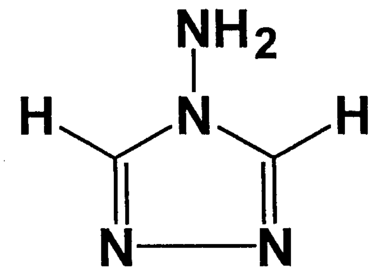
- significantly higher densities
- negligible vapor pressure at working conditions
- significantly lessened toxicities resulting in ease of handling
- tremendous Isp increases over hydrazine

<u>Shortcomings:</u>

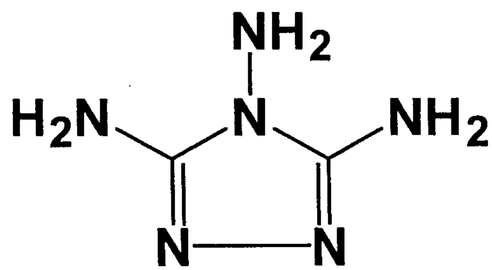
- compatibility issues with many materials
- meeting the 1.3 explosive classification versus the 1.1 explosive classification
- extremely high temperatures during combustion
- catalyst compatibility and reactivity



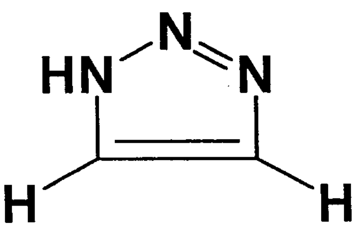
1-H-1, 2, 4-triazole
ΔHf (est) = +47 kcal/mole



4-amino-1, 2, 4-triazole
ΔH_f (est) = +76 kcal/mole



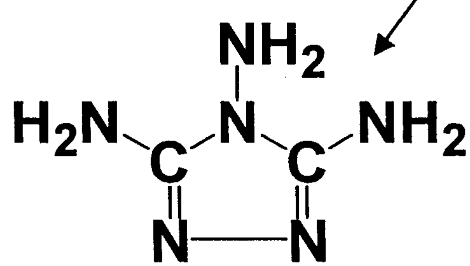
3, 4, 5-triamino-1, 2, 4-triazole
ΔH_f (est) = +56 kcal/mole



1-H-1, 2, 3-triazole
ΔHf (est) = + 65 kcal/mole

Synthesis of 3,4,5-triamino-1,2,4-triazole

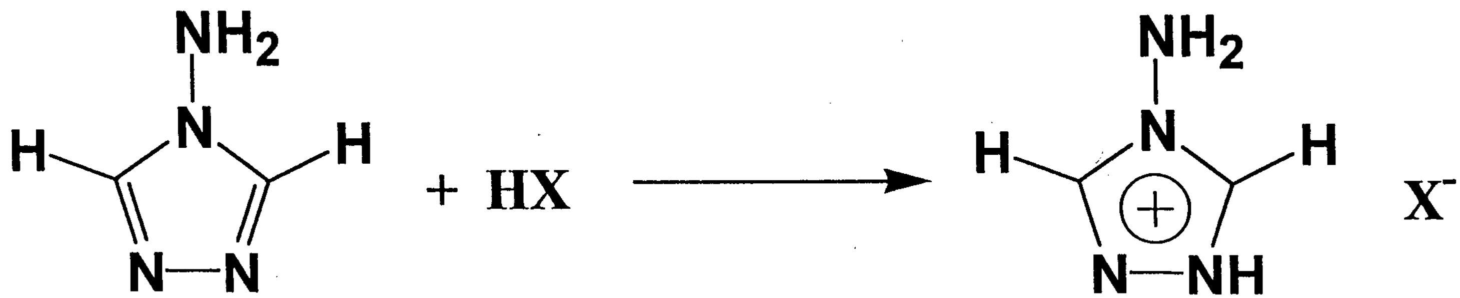
$$2\ N_2H_4 + 2\ (CH_3)_2N\text{-}CN \longrightarrow 2\ [NH_2\text{-}NH\text{-}CN] + 2\ (CH_3)_2NH$$



White crystalline solid; melting point of 277°C

Child, R. G. J. Heterocycl. Chem. **1965**, *2*, 98.

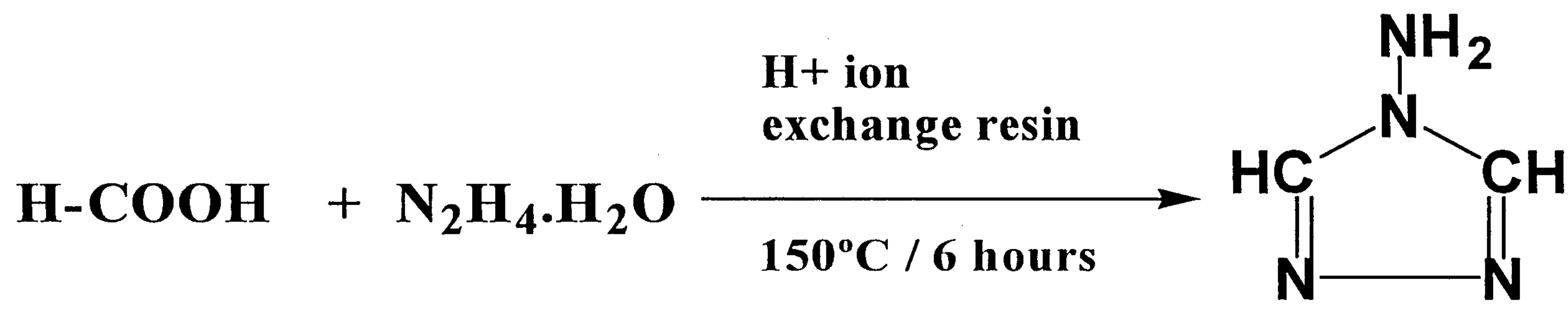
<u>Energetic Salts made from 3, 4, 5-triamino-1, 2, 4-triazole</u>



Where HX = HNO_3, $HClO_4$
"$HN(NO_2)_2$"

Physical Property	3, 4, 5-amino-1, 2, 4-triazolium nitrate	3, 4, 5-amino-1, 2, 4-triazolium perchlorate	3, 4, 5-amino-1, 2, 4-triazolium dinitramide
Melting point	205°C	198°C	145°C
DSC decomp onset	255°C	>300°C	150°C
Impact sensitivity	> 200 kgcm	50 kgcm	196 kgcm!
Friction sensitivity	16 kg	15.2 kg	15.2
TGA studies @ 75°C	0.2% / 1 day PASS	0.01 % / 1 day PASS	0.134 % / 1 day PASS

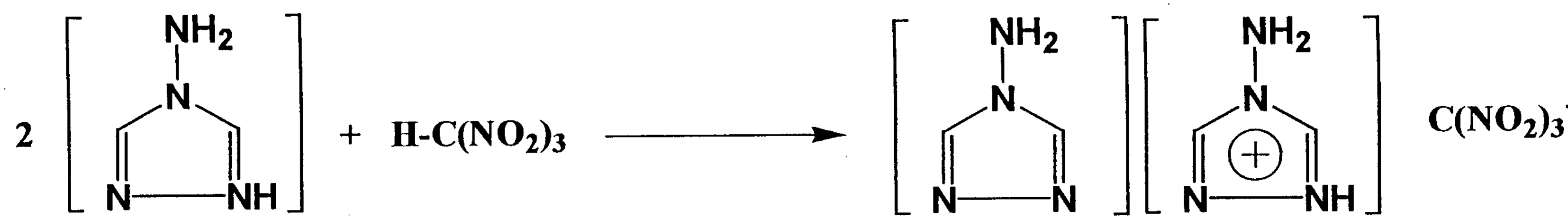
Synthesis of 4-amino-1,2,4-triazole (4-AT)



White, crystalline solid
Melting point 87-89°C
High yield = 90%
ΔH_f = +76 kcal/mole (estimate)

Goe, Gerald, L. ; Scriven, Eric, F. V. ; Keay, James, G. ; Huckstep, Lowell, M. U. S. Patent 5,099,028, March 24, 1992.

Russians have reported several energetic complexes of substituted 4-amino-1, 2, 4-triazoles with trinitromethane, including the parent heterocycle in 1966.



Orange, hygroscopic solid, m.p. 95°C was reported, no other energetic salts were mentioned.

Slovetskii, V. I. ; Brusnikina, V. M. ; Khmel'nitskii, L. I. ; Lebedev, O. V. ; Novikov, S. S. Khim. Geterotsikl. Soedin. 1966, 2, 448.

Energetic Salts made from 4-amino-1, 2, 4-triazole

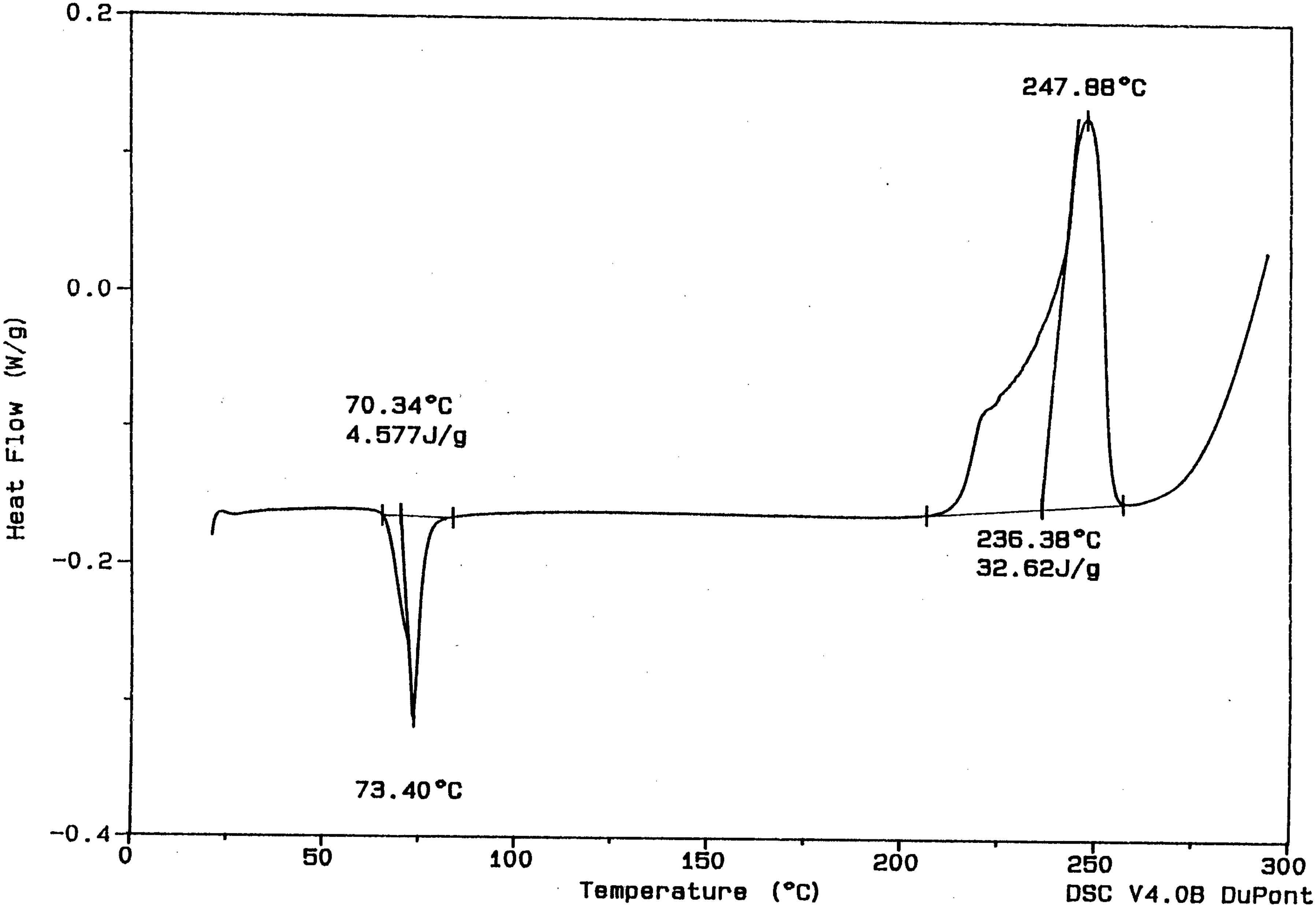
Where HX = HNO_3
$HClO_4$
"$HN(NO_2)_2$"

Physical Property	4-amino-1, 2, 4-triazolium nitrate	4-amino-1, 2, 4-triazolium perchlorate	4-amino-1, 2, 4-triazolium dinitramide
Melting point	69°C	73°C	20°C
DSC decomp onset	180°C	210°C	146°C
Impact sensitivity	> 200 kgcm	30 kgcm	< 5 kgcm!
TGA studies @ 75°C	0.58% / 1 day PASS	0.02 % / 1 day PASS	0.29 % / 1 day PASS

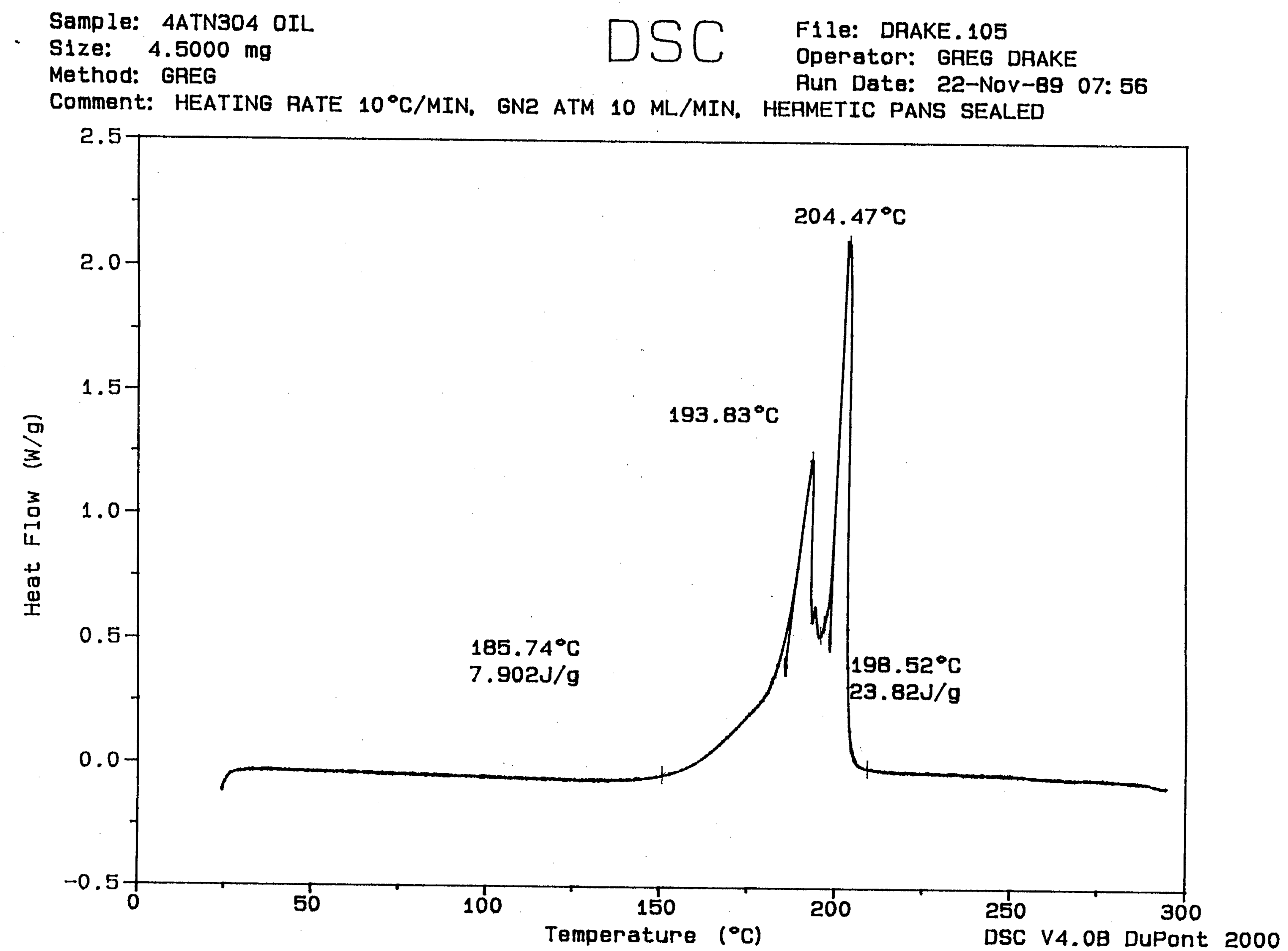
Sample: CRYSTALLINE 4-ATCLO4
Size: 3.0000 mg
Method: GREG
Comment: HEATING RATE 10°C/MIN, GN2 ATM 10 ML/MIN, HERMETIC PANS SEALED

DSC

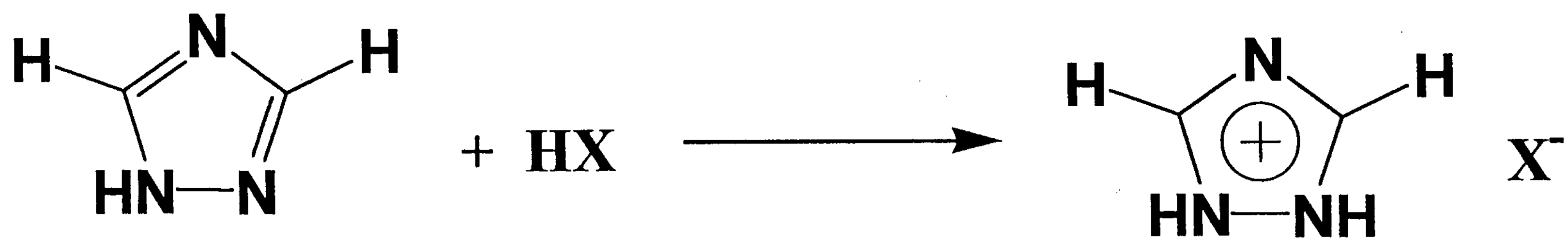
File: DRAKE.100
Operator: greg
Run Date: 14-Nov-89 11: 45



DSC V4.0B DuPont 2000


Sample: 4ATN304 OIL
Size: 4.5000 mg
Method: GREG
Comment: HEATING RATE 10°C/MIN, GN2 ATM 10 ML/MIN, HERMETIC PANS SEALED
DSC
File: DRAKE.105
Operator: GREG DRAKE
Run Date: 22-Nov-89 07:56
204.47°C
193.83°C
185.74°C
7.902J/g
198.52°C
23.82J/g
Heat Flow (W/g)
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
50
100
150
200
250
300
Temperature (°C)
DSC V4.0B DuPont 2000

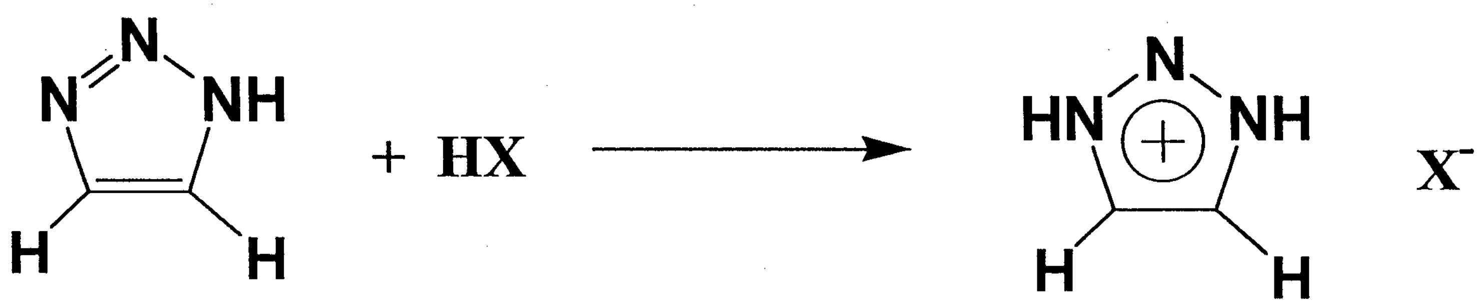
Energetic Salts of 1, 2, 4-triazole which were synthesized



Where HX = HNO_3
$HClO_4$
"$HN(NO_2)_2$"

Physical Property	1, 2, 4-triazolium nitrate	1, 2, 4-triazolium perchlorate	1, 2, 4-triazolium dinitramide
Melting point	137°C	89°C	75°C
DSC decomp. onset	182°C	185°C	120°C
Impact sensitivity	> 200 kg cm	114 kg cm	98 kg cm
TGA studies @ 75°C	0.88 % / 1 day PASS	0.03% / 1 day PASS	1.62 % / 1 day FAIL

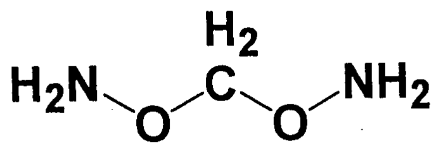
Energetic salts made from 1, 2, 3-triazole

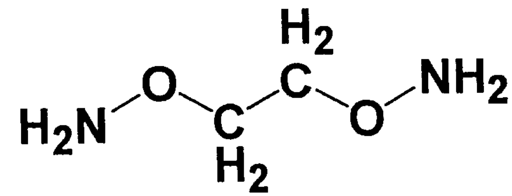


Where HX = HNO_3
$HClO_4$
"$HN(NO_2)_2$"

Physical Property	1, 2, 3-triazolium nitrate	1, 2, 3-triazolium perchlorate	1, 2, 3-triazolium dinitramide
Melting point	110°C	73°C	61°C
DSC decomp onset	125°C	200°C	80°C
Impact sensitivity	> 200 kgcm	15 kgcm	Not tested
TGA studies @ 75°C	73.5 % / 1day FAIL	0.05% / 1day PASS	Low decomp. temp

Ethylene bisxoyamine versus methylene bisoxyamine?



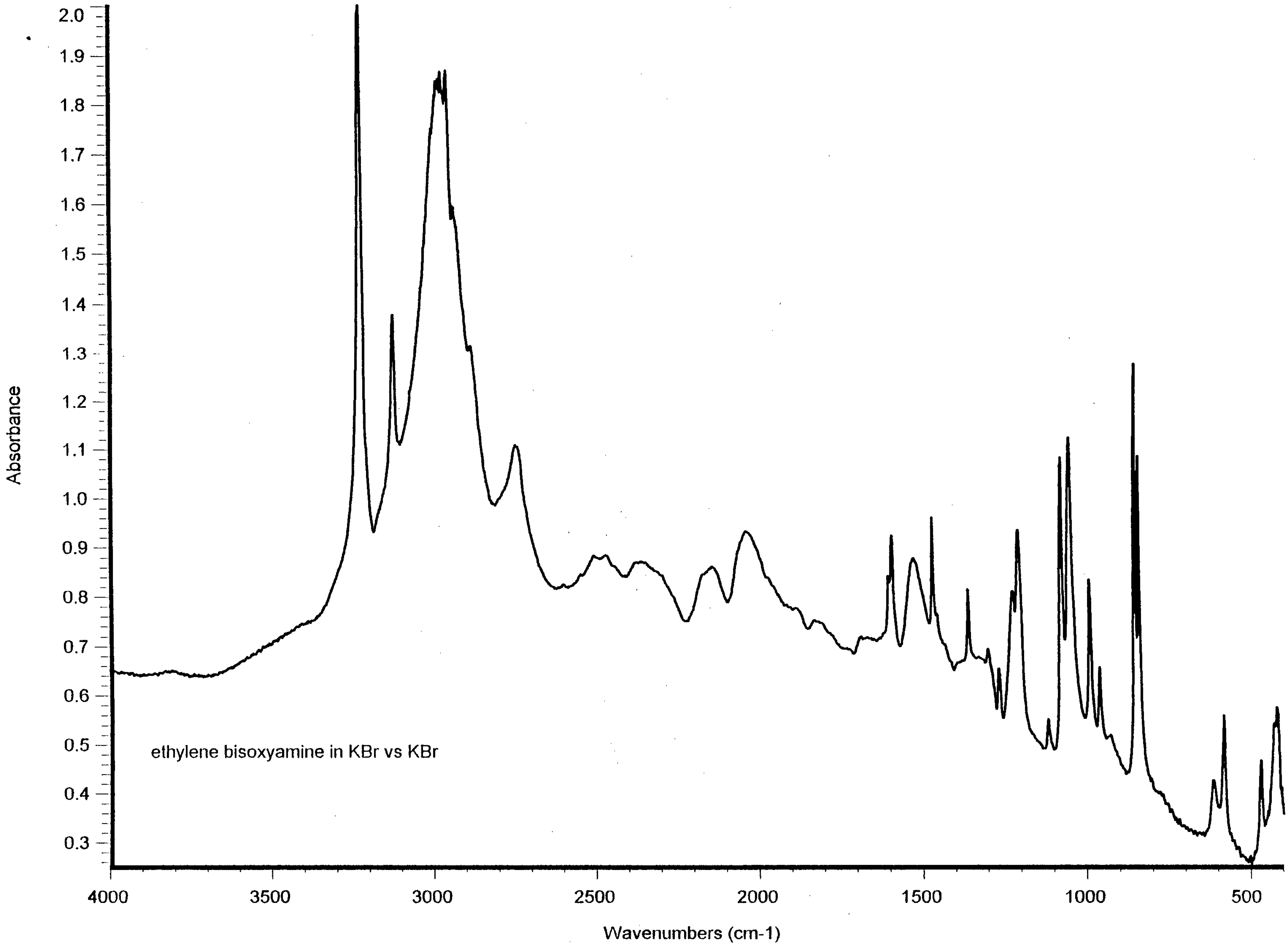


Physical property	$CH_2(\text{-O-}NH_2)_2$	$NH_2\text{-O-}CH_2\text{-}CH_2\text{-O-}NH_2$
Melting point	0° C	125°C
DSC onset (decomposition)	125° C	Right after melt
Δ H formation (estimate)	-20 kcal/mole	-24 kcal/mole

Experience with methylene bisoxyamine salts has not been good

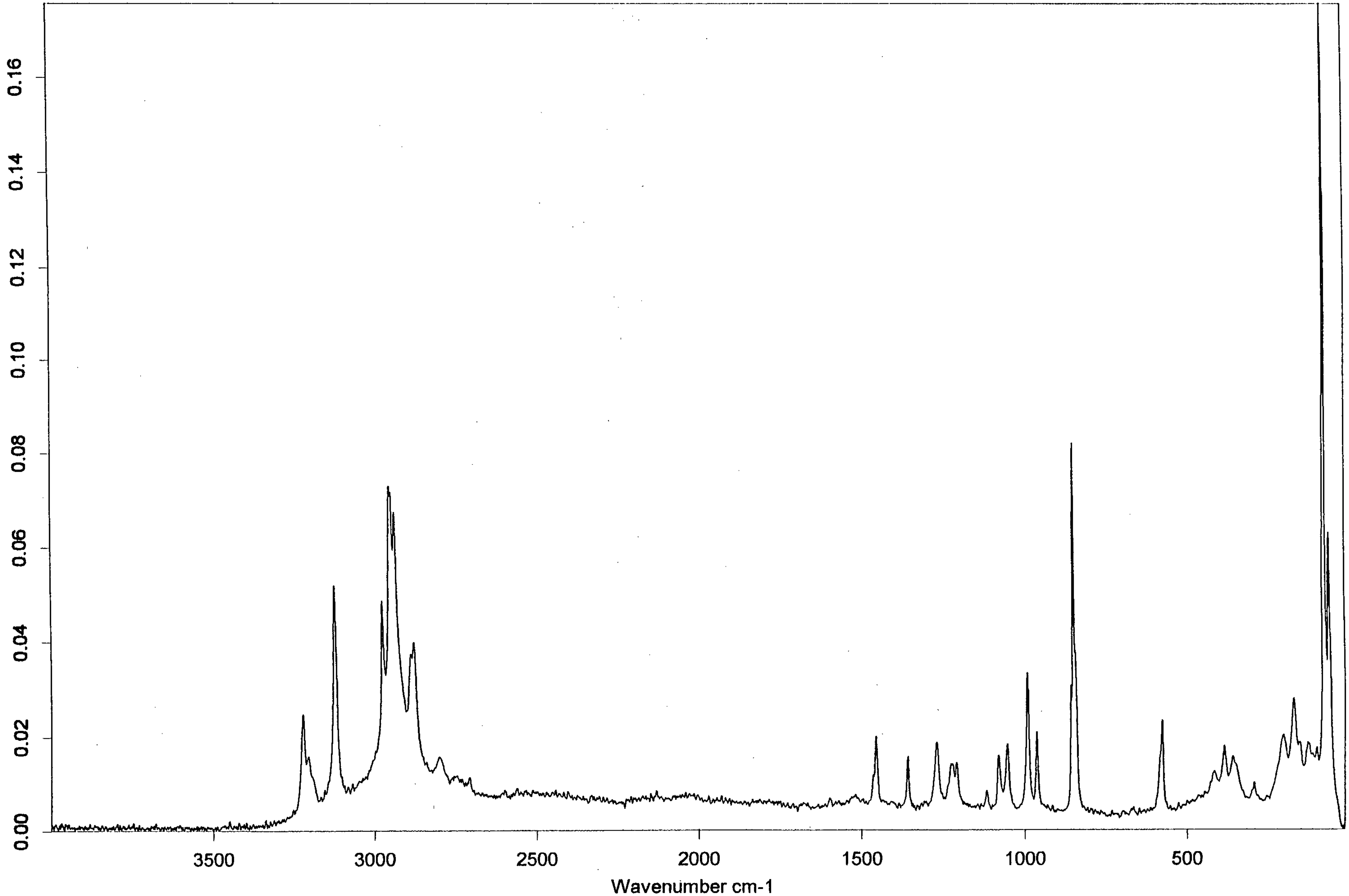
- poor thermal stability, both mono and bis salts
- double salts have had unexpected deflagrations

Could there be a difference between geminal and monooxyamine salts?


Absorbance
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
ethylene bisoxyamine in KBr vs KBr
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

Sample: ethylene bisoxyamine xstals in mp capillary
Sample Source: Signal to noise, big aperture
Laser Power : 800

Date Recorded: 10/ 8/2000
Time Recorded: 14:30:57



greg
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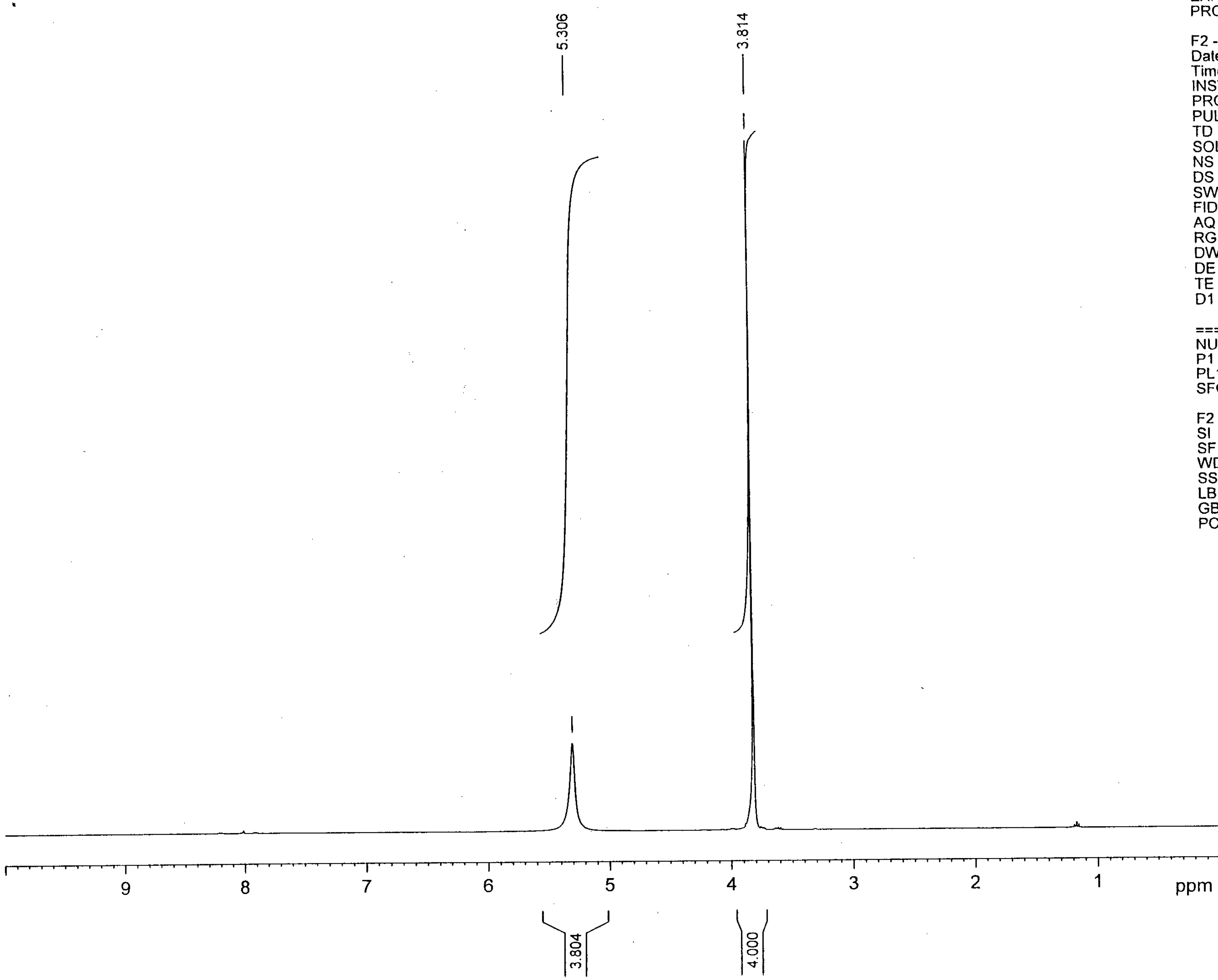
HEDM/PRS
EQUINOX 55

Sample Scans 40
Raman Laser Wavenumber 9394

ethylene bisoxyamine second run in CD3OD



Current Data Parameters

NAME	etonh22
EXPNO	1
PROCNO	1

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PULPROG	zg30
TD	65536
SOLVENT	MeOH
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	12.7
DW	60.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

============ CHANNEL f1 ===

NUC1	1H
P1	7.20 usec
PL1	-6.00 dB
SFO1	400.1324710 MHz

F2 - Processing parameters

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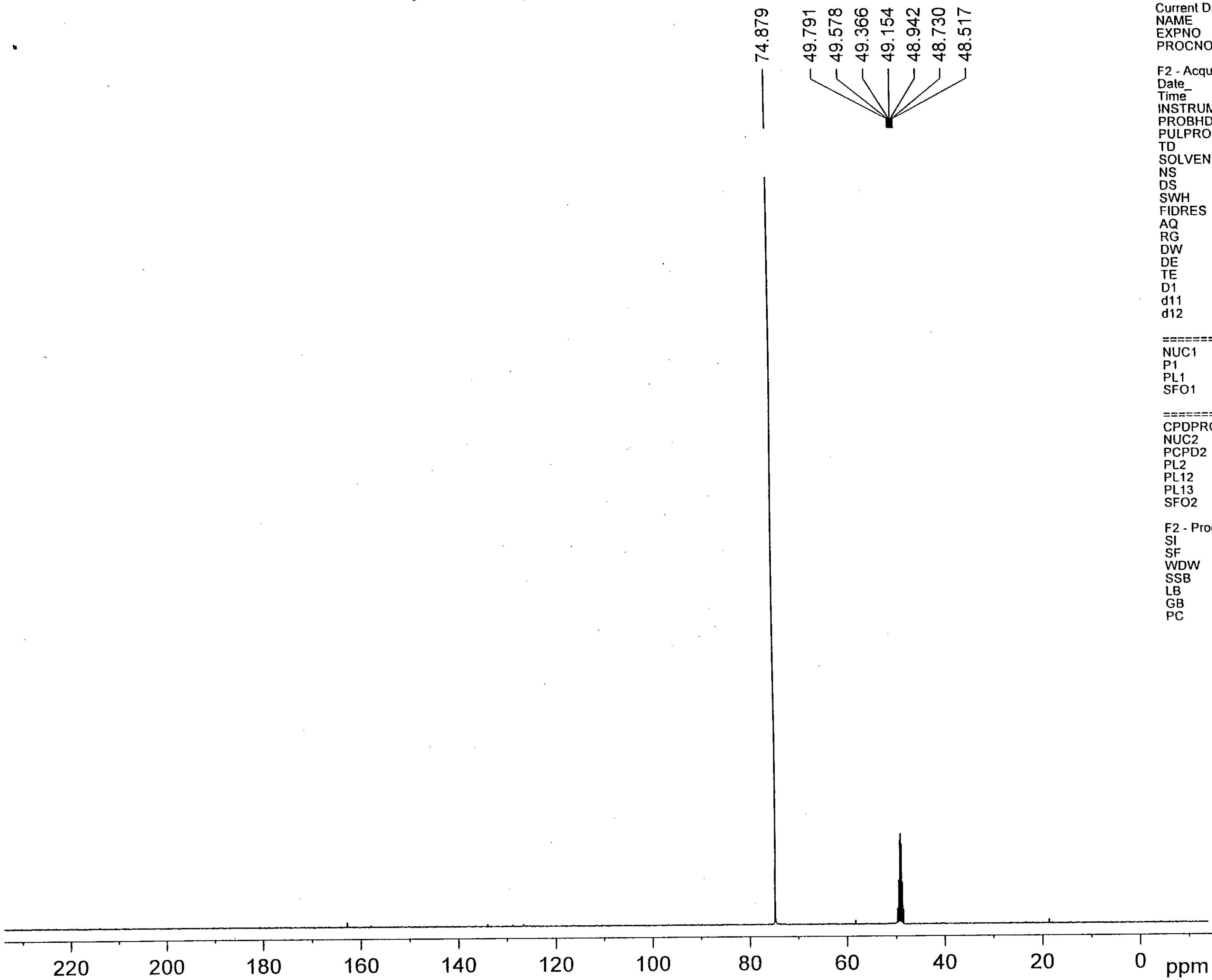
ethylene bisoxyamine second run in CD3OD



Current Data Parameters
NAME etonh22
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
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Time 16.16
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT MeOH
NS 125
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 8192
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

============ CHANNEL f1 =====
NUC1 13C
P1 7.00 usec
PL1 -5.00 dB
SFO1 100.6237959 MHz

============ CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 18.50 dB
PL12 18.00 dB
PL13 120.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6126284 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

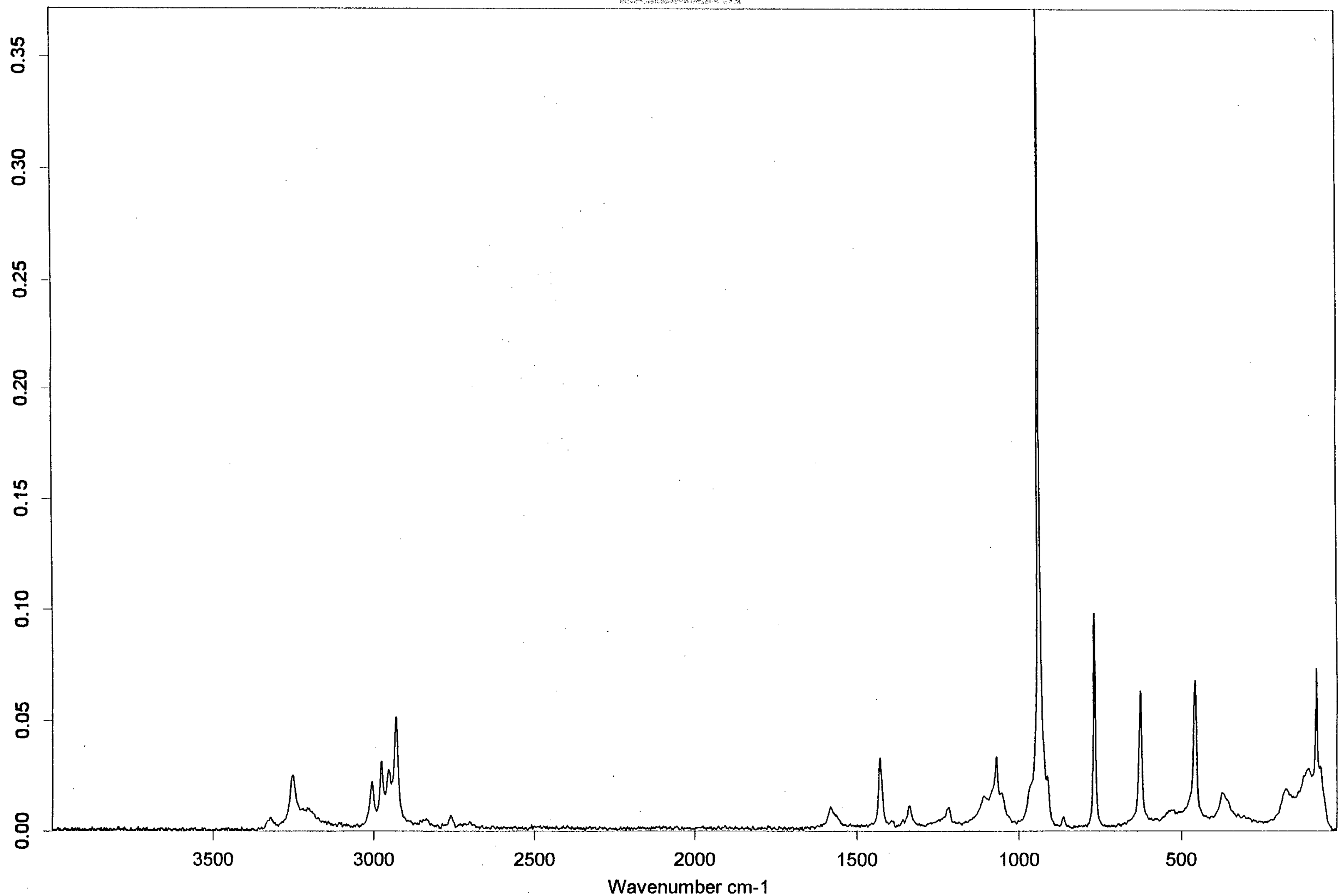
Single salts of ethylene bisoxyamine

Physical Property	1, 2-bisoxyamino-ethane NO_3^-	1, 2-bisoxyamino-ethane ClO_4^-	1, 2-bisoxyamino-ethane $N(NO_2)_2^-$
Melting point	76° C	137° C	59° C
DSC onset	100° C	140° C (after melt)	75-80° C
Impact sensitivity	94 kg cm	<< 10 kg cm	28 kg cm
Friction sensitivity	22.8 kg	< 0.45 kg	1.5 kg
Thermal stability At 75° C			

Ethylene bisoyxamine mono salts are very sensitive materials!
Friction/impact tests were very "positive" with loud reports and destroyed tools!

Sample: ethylene bisoxyamine monoperchlorate crystals
Sample Source: Signal to noise, big aperture
Laser Power : 800

Date Recorded: 29/ 9/2000
Time Recorded: 12:54: 9



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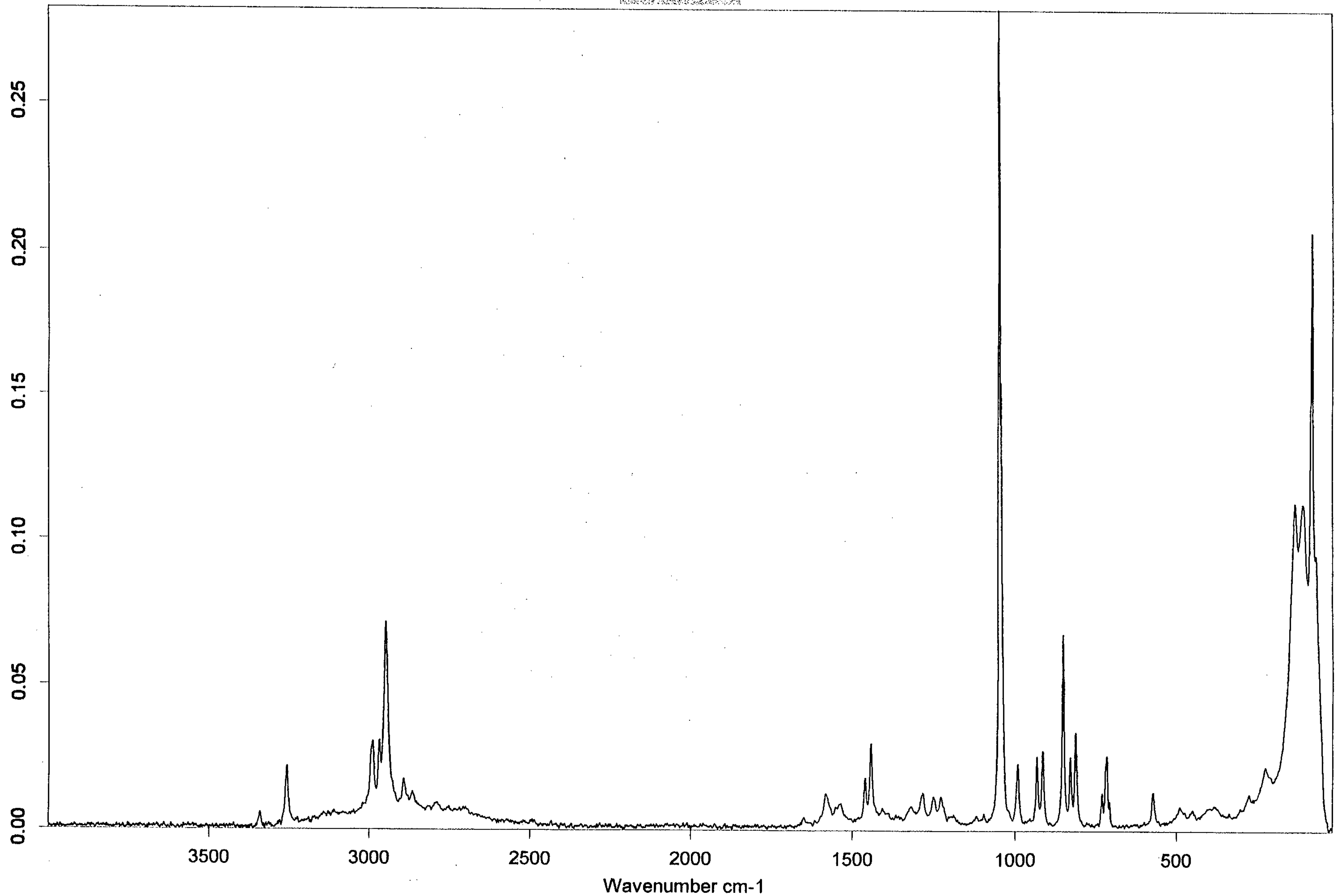
EQUINOX 55

Sample Scans 40
Raman Laser Wavenumber 9394

Sample: ethylene bisoxyamine mononitrate crystals
Sample Source: Signal to noise, big aperture
Laser Power : 600

Date Recorded: 29/ 9/2000
Time Recorded: 12:46:17



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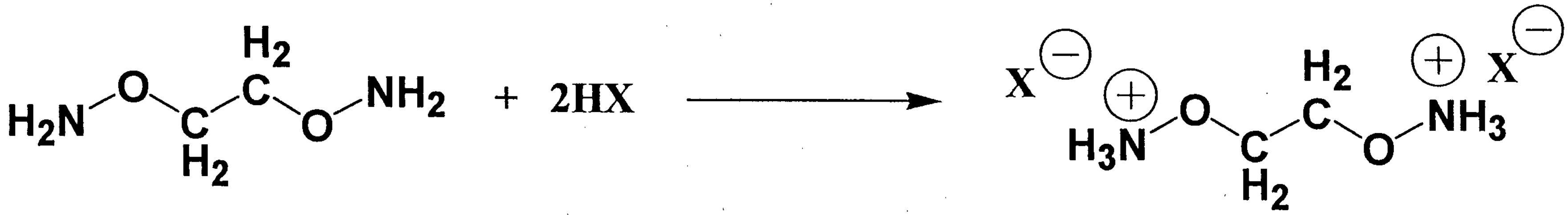
HEDM/PRS
EQUINOX 55

Sample Scans 40
Raman Laser Wavenumber 9394

Double salts of ethylene bisoxyamine

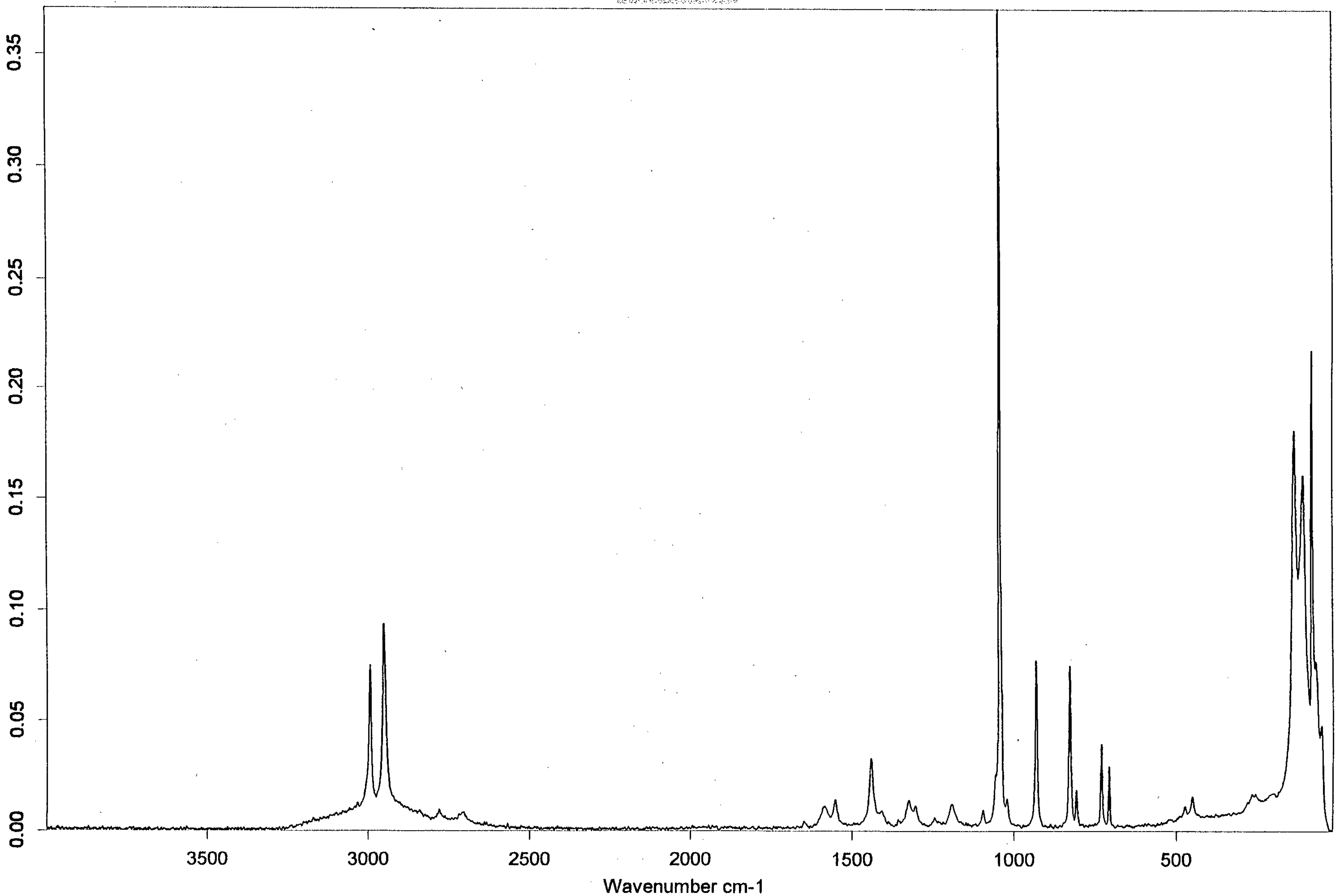


Physical Property	1, 2-bisoxyamino-ethane $[NO_3^-]_2$	1, 2-bisoxyamino-ethane $[ClO_4^-]_2$	1, 2-bisoxyamino-ethane $[N(NO_2)_2^-]$
Melting point	135° C	123° C	° C
DSC onset	165° C	192° C	° C
Impact sensitivity	188 kg cm	<< 10 kg cm	<< 10 kg cm
Friction sensitivity	9.6 kg	< 0.45 kg	<< 0.45 kg
Thermal stability At 75° C			

Double salt of ethylene bisoxyamine don't decompose when they melt like mono salts or any methylene bisoxyamine salt. However, the safety properties are scary!

Sample: EBO dinitrate salt (recrystallized) in a mp capillary
Sample Source: Signal to noise, big aperture
Laser Power : 600

Date Recorded: 3/ 8/2000
Time Recorded: 14:21:27



greg
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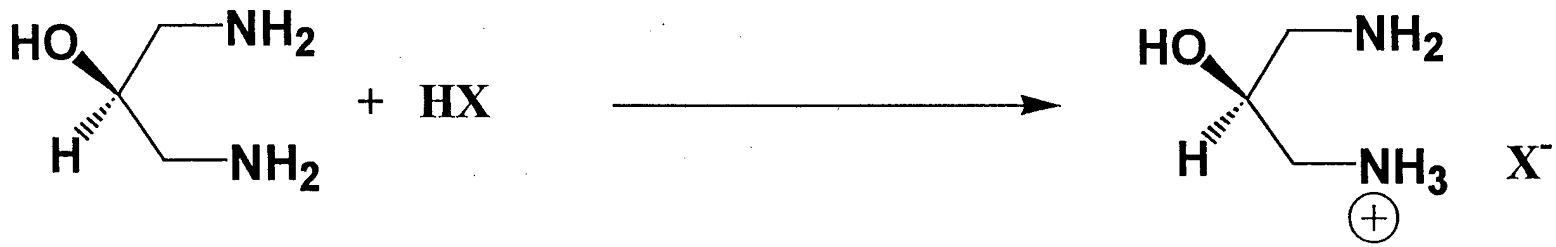
EQUINOX 55

Sample Scans 40
Raman Laser Wavenumber 9394

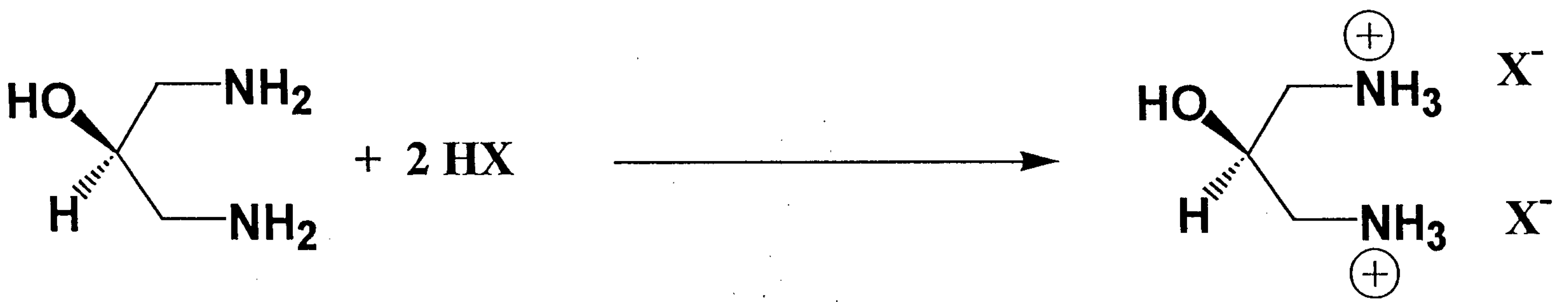
Single Salts of 1, 3-diamino-2-propanol



Where HX = HNO_3, $HClO_4$, "$HN(NO_2)_2$"

Physical Property	1, 3-diamino-2-propanol mononitrate	1, 3-diamino-2-propanol monoperchlorate	1, 3-diamino-2-propanol monodinitramide
Melting point	56 °C	84 °C	76 °C
DSC decomp. onset	250°C	225 °C	120 °C
Impact sensitivity	kgcm	kgcm	kgcm
Friction sensitivity	kg	kg	kg
TGA @ 75°C	< 1% / day (PASS)	< 1% / Day (PASS)	?

Double Salts of 1, 3-diamino-2-propanol



Where HX = HNO_3, $HClO_4$, "$HN(NO_2)_2$"

Physical Property	1, 3-diamino-2-propanol dinitrate	1, 3-diamino-2-propanol diperchlorate	1, 3-diamino-2-propanol bisdinitramide
Melting point	122°C	142°C	76°C
DSC decomp. onset	225°C	250°C	130°C
Impact sensitivity	> 200 kgcm	66 kgcm	45 kgcm
Friction sensitivity	22.8 kg	2.2 kg	5.1 kg
TGA @ 75°C	< 1% / day (PASS)	< 1% / Day (PASS)	?

Summary and Conclusions

Synthesis and characterization of wide array of simple heterocyclic salts involving 1, 2, 4-triazole, 1, 2, 3- triazole, 4-amino-1, 2, 4-triazole, and 3, 4, 5-triamino-1, 2, 4-triazole and the energetic anions of nitrate, perchlorate, and dinitramide was completed. There was a wide array of physical and safety properties amongst these heterocycles. Most passed the stiff Air Force requirements demanded of new monopropellant ingredients. Other N-amino heterocycles are being looked at for future work in energetic salt synthesis.

Synthesis and characterization of several energetic salts of ethylene bisoxyamine was carried out. Both the 1:1 and 1:2 salts of this highly energetic molecule had some of the desired properties for new salts, including low melt points, and ease of synthesis. However, most had poor thermal stabilities, and possessed frightening safety properties. Apparently, having separated, multiple oxyamine functional groups in a compound, does not improve either physical or safety properties. Careful consideration will be used in the future synthesis of any multiple oxyamine containing material.

The synthesis and characterization of energetic salts of 1, 3-diamino-2-propanol was completed. This family of salts had low melting points, but with high DSC onsets, as was expected. Many of the new materials have excellent thermal stability at elevated temperatures and good safety properties. Work is continuing with this family of materials, and similar materials are being currently sought.

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